

Rare case of magnetic Ag^{3+} ion: double perovskite Cs_2KAgF_6

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Normally $4d$ or $5d$ transition metals are in a low-spin state. Here using first-principles calculations, we report on a rare case of a high-spin $S=1$ magnetic state for the Ag^{3+} ion in the double perovskite Cs_2KAgF_6 . We also explored a possibility of a conventional low-spin $S=0$ ground state and find an associated tetragonal distortion to be 0.29 \AA . However, the lattice elastic energy cost and the Hund exchange loss exceed the e_g crystal-field energy gain, thus making the low-spin tetragonal structure less favorable than the high-spin cubic structure. We conclude that the compact perovskite structure of Cs_2KAgF_6 is an important factor in stabilizing the unusual high-spin ground state of Ag^{3+} .

I. INTRODUCTION

Transition metal compounds possess diverse properties, largely due to their electronic correlation effects and the interplay of charge, spin, and orbital degrees of freedom. For many of them, spin state is an important issue. It can be a high-spin (HS), low-spin (LS), or even an intermediate-spin (IS) state. The corresponding electronic configurations, e.g., for a Fe^{3+} ion in an octahedral crystal field, are $t_{2g}^3 e_g^2$, t_{2g}^5 , and $t_{2g}^4 e_g^1$. The spin state is intimately related to materials properties such as magnetic transitions, metal-insulator transition, and transport behavior. In the past decades, a lot of research has been carried out on the spin state of $3d$ transition-metal compounds [1–8]. A consensus has been reached that the spin state issue arises mainly from a competition between the Hund's rule coupling and crystal-field splitting. The former favors a HS state, and the later a LS state. Compared to the well studied spin state issue of $3d$ transition metals, little research has been done on the spin state of $4d/5d$ transition-metal compounds[9, 10], which is probably due to a fact that in most cases, $4d/5d$ transition metals are in a LS state. As $4d/5d$ orbitals are spatially more extended than $3d$ ones, their stronger interaction with the anionic ligands and a larger crystal-field splitting but a moderate or weak Hund exchange normally stabilize the LS state[9, 10].

In this work, we have studied the double perovskite Cs_2KAgF_6 using first-principles calculations, focusing on its exotic spin state. Fig. 1 shows its cubic structure, in which K^+ and Ag^{3+} ions form an ordered arrangement on the B -sites of the perovskite ABF_3 [11, 12], and the Ag-F bond distance is 2.13 \AA (see also the structural parameters in Table I). Although a Ag^{3+} ion ($4d^8$) could in principle be either in a LS state ($S=0$, $t_{2g}^6(3z^2 - r^2)^2(x^2 - y^2)^0$) or in a HS state ($S=1$, $t_{2g}^6(3z^2 - r^2)^1(x^2 - y^2)^1$), in reality almost in all known cases

the Ag^{3+} ion is in the LS state and is thus nonmagnetic[13]. Actually, very few Ag^{3+} and Cu^{3+} (both with d^8 electronic configuration) crystalline compounds are known. These compounds mostly have a tetragonal or lower symmetry structure to maintain the LS $S=0$ ground state[14]. Similar to the well-known Jahn-Teller (JT) ions like Cu^{2+} and Ag^{2+} , the Cu^{3+} and Ag^{3+} ions could have an even stronger tendency to JT-driven distortions (local elongation of ligand octahedra). Such distortions are usually so strong that the corresponding energy gain exceeds the intraatomic Hund's exchange energy, thus stabilizing the LS state. Indeed, the energy of the state with the tetragonal distortion u can be written as

$$E = -gnu + Bu^2/2, \quad (1)$$

where g is the JT coupling constant determining the splitting of the originally degenerate e_g levels with the distortion, and n is the number of electrons or holes on the e_g levels (in our case $n = 2$, in contrast to $n = 1$ (one hole) in the more familiar ion Cu^{2+} (d^9)). The second term on the right of the above equation corresponds to lattice elastic energy. Minimizing this equation with respect to the distortion u , we get the equilib-

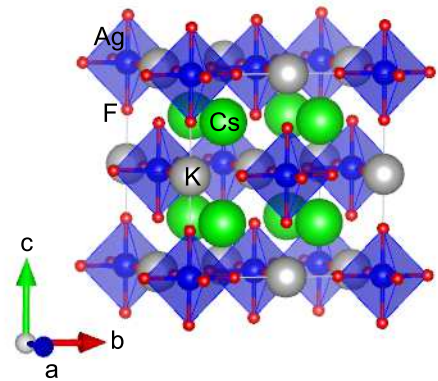


FIG. 1: (color online) Double perovskite structure of Cs_2KAgF_6 .

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TABLE I: The lattice parameters of Cs_2KAgF_6 in the experimental cubic structure[11], and in the optimized tetragonal and ac-tetragonal phases.

phases	cubic	tetragonal	ac-tetragonal
space group	$Fm\bar{3}m$	$I4/mmm$	$I4/mmm$
a (Å)	9.175	6.488	6.195
b (Å)	9.175	6.488	6.195
c (Å)	9.175	9.175	10.062
x,y,z (Cs)	(0.75, 0.25, 0.25)	(0, 0.5, 0.25)	(0, 0.5, 0.25)
x,y,z (K)	(0.5, 0, 0)	(0, 0, 0)	(0, 0, 0)
x,y,z (Ag)	(0, 0, 0)	(0, 0, 0.5)	(0, 0, 0.5)
x,y,z (F)	(0, 0, 0.232)	(0.213, 0.213, 0.5)	(0.224, 0.224, 0.5)
		(0, 0, 0.745)	(0, 0, 0.724)

rium distortion

$$u_0 = gn/B, \quad (2)$$

so that the energy minimum is

$$E_0 = -g^2 n^2 / 2B. \quad (3)$$

Thus we see that the decrease of the energy for the ions like Cu^{3+} and Ag^{3+} with $n = 2$ is *four times as large as* in the already strong JT ions like Cu^{2+} . In effect this energy almost always exceeds the on-site Hund's exchange energy J_H , and such ions have a very strong tendency to such distortion and to the nonmagnetic LS state.

Although Cs_2KAgF_6 was not much studied, the available magnetic susceptibility and crystal structure data both suggest a HS state for the Ag^{3+} ion[11, 12]. It is indeed very surprising that Cs_2KAgF_6 has magnetic Ag^{3+} ions and these ions sit in the undistorted F_6 octahedra. Why is this the case, which physical mechanisms determine this and what is so specific for this particular material, require explanation. Better understanding of this could open possibilities to stabilize strange states like "magnetic silver" or "magnetic gold" in some other situations. Clarification of the physics leading to such unusual situation is the main goal of the present investigation. Our first-principles calculations indeed show that the undistorted magnetic HS state of Ag^{3+} in Cs_2KAgF_6 is the lowest energy state, and the more conventional JT-distorted LS state lies much higher in energy. The detailed analysis of our results demonstrates that the compact perovskite structure of Cs_2KAgF_6 could allow only a moderate tetragonal distortion for the LS state, due to a large elastic energy cost associated with the "hard lattice". Then the moderate e_g crystal-field energy gain is not sufficient to compensate for the elastic energy cost and the Hund's exchange loss. As a result, the LS state cannot be stabilized as a ground state. Therefore, Cs_2KAgF_6 is in the HS ground state and represents a rare case of the magnetic Ag^{3+} ion.

II. COMPUTATIONAL DETAILS

We have used the experimental cubic structure of Cs_2KAgF_6 and the optimized tetragonal structures, see Table

TABLE II: The relative total energies ΔE (meV/fu), band gap E_g (eV) and e_g orbital occupation (up/down) of Cs_2KAgF_6 in different states calculated by LSDA+ U . The t_{2g} orbitals are fully occupied in all cases and omitted here. The cubic HS state is the ground state.

State	ΔE	E_g	$3z^2 - r^2$	$x^2 - y^2$
cubic HS	0	1.12	0.95/0.48	0.95/0.48
tetragonal LS	366	0.11	0.94/0.94	0.49/0.49
tetragonal HS	441	0.03	0.94/0.47	0.97/0.45
ac-tetragonal LS	336	0.23	0.94/0.94	0.49/0.49

I. All the calculations were performed using the full-potential augmented plane wave plus local orbital method (Wien2k) [15]. The muffin-tin sphere radii were chosen to be 2.8, 2.5, 2.2, and 1.4 bohr for Cs, K, Ag and F atoms, respectively. The cutoff energy of 16 Ryd was used for plane wave expansion. The calculations were fully converged using 300 k points in the first Brillouin zone. Exchange and correlation effects were taken into account in a local spin density approximation (LSDA)[16]. All the calculations were performed in a ferromagnetic state unless otherwise specified (Actually, Cs_2KAgF_6 could well be paramagnetic, see the results below). To account for the strong electron correlations, we performed LSDA+ U calculations[17], where $U_{eff} = U - J$ (U and J are on-site Coulomb interaction and exchange interaction, respectively) was used instead of U [18]. And the orbital-dependent potential has the form of $\Delta V = -U_{eff}(\hat{n}^\sigma - \frac{1}{2}I)$ [19], where \hat{n}^σ is the orbital occupation matrix of spin σ . This type of double-counting correction is made in a fully localized limit[20, 21]. In particular, LSDA+ U method allows us to access different spin and orbital states by initializing their corresponding density matrix. We find that the calculated results change insignificantly for the U_{eff} value in the range of 3-5 eV (which is a reasonable choice according to previous studies on the electronic structure of Cs_2AgF_4 [22, 23]): The cubic HS state is constantly more stable than the tetragonal LS state by more than 300 meV/fu (see Table II for $U_{eff} = 4$ eV), and the HS-LS relative energy varies within only 10 meV/fu for $U_{eff} = 3-5$ eV. Correspondingly, with the increase of U_{eff} from 3 to 5 eV, the insulating gap increases from 0.97 to 1.27 eV, and the local Ag spin moment from 0.94 to 0.97 μ_B . To further confirm our LSDA+ U results, we also performed hybrid functional PBE0 calculations [24, 25], in which 1/4 Fock exact exchange is mixed into the PBE exchange functional. Our PBE0 results show that the cubic HS state is more stable than the tetragonal LS state by about 600 meV/fu, and the HS ground state has an insulating gap of 1.48 eV and the local Ag spin moment of 1.06 μ_B . All these results indeed (qualitatively) confirm the LSDA+ U results. As such, below we focus on the results obtained with $U_{eff} = 4$ eV.

III. RESULTS AND DISCUSSION

To see first the nature of Ag-F interaction, a spin-polarized LSDA calculation is performed for the cubic structure of Cs_2KAgF_6 in a ferromagnetic state. We also calculated an an-

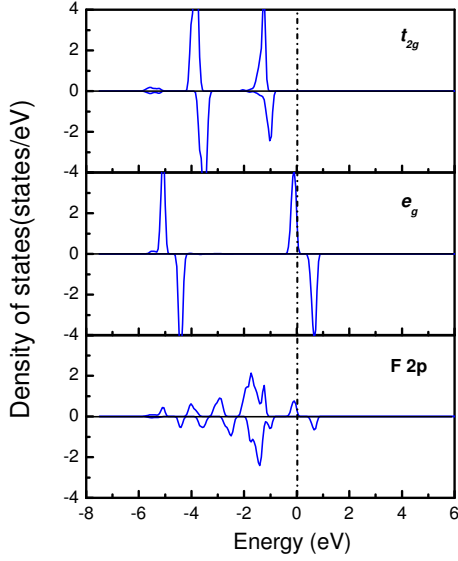


FIG. 2: (color online) The density of states of Ag-4d and F-2p orbitals for the cubic phase of Cs_2KAgF_6 by LSDA.

tiferromagnetic state and find that the exchange between two nearest-neighboring Ag ions is weakly antiferromagnetic, being only about 1 meV. The electronic structures of the ferromagnetic and antiferromagnetic states are practically the same. Considering a magnetic frustration associated with the FCC sublattice of the Ag ions, a paramagnetic state, or a spin glassy one below very low temperature (few K) can be expected for Cs_2KAgF_6 . Our LSDA calculations show that it is an insulator with a band gap of 0.5 eV given by the e_g exchange splitting, see Fig. 2. Besides the common t_{2g} - e_g crystal-field splitting, there is a large bonding-antibonding splitting due to the strong Ag 4d-F 2p covalency, being about 5 and 3 eV for the e_g and t_{2g} orbital, respectively. As a result, the e_g bonding state is even lower than the t_{2g} one[26]. The t_{2g} bands are fully occupied and the e_g bands are 3/4 occupied, with the fully occupied up-spin t_{2g} and e_g channels. This demonstrates the existence of a HS state and a $d^9\bar{L}$ configuration for the formal Ag^{3+} (d^8) ion. The one hole spreads over the six F atoms in the AgF_6 unit, which accounts for a reduced spin moment of $0.90 \mu_B$ on the Ag site and a finite spin moment of $0.16 \mu_B$ on each F. Summing up of all these moments and a small fraction in the interstitial region gives a total integer spin moment of $2 \mu_B/\text{fu}$, confirming the formal HS $S=1$ state for the Ag^{3+} ion. As these magnetic AgF_6 units are separated in this double perovskite by the corner-shared KF_6 units, they form narrow bands (sharp DOS curves) and are weakly antiferromagnetically coupled.

Late 4d transition-metal oxides or fluorides often have a moderate electron correlation. As Cs_2KAgF_6 is a narrow band system, it is natural to study its electron correlation effect. In the following, we carried out LSDA+ U calculations to study the electron structure of Cs_2KAgF_6 and its spin state. By a comparison of Figs. 3 and 2, we see that with inclusion of the Hubbard's interaction U the Ag 4d states undergo some changes, and the biggest effect is that the band gap is in-

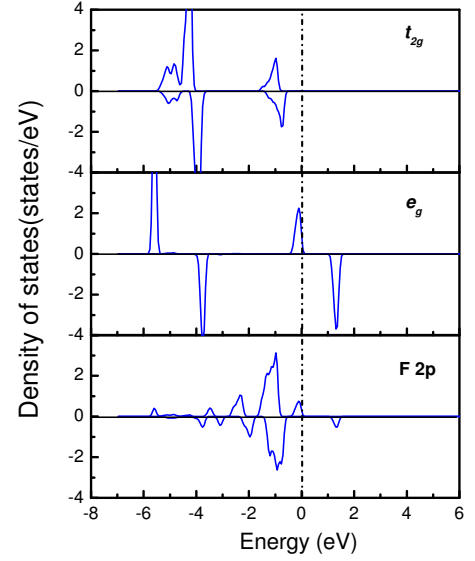


FIG. 3: (color online) The density of states of Ag-4d and F-2p orbitals for the cubic phase of Cs_2KAgF_6 by LSDA+ U .

creased from 0.5 eV by LSDA to 1.1 eV by LSDA+ U . The HS $S=1$ state remains, and the strong Ag-F covalency is reflected again by the occupied bonding state of the otherwise empty down-spin e_g orbital. It is the covalent electron occupation of $0.48e \times 2$ (see Table II) that accounts for the actual configuration $d^9\bar{L}$ of the formal Ag^{3+} ion which is a negative charge transfer cation[14].

The above HS magnetic state of the formal Ag^{3+} ion seems to be a straightforward result, but it is actually quite unusual as 4d transition metals are normally in a LS state and the Ag^{3+} is indeed in the LS state for almost all known cases[13]. We are thus motivated to check whether there exists another stable structural phase for Cs_2KAgF_6 in which the normal LS state could become a ground state. For this purpose, we have also studied a tetragonal structure and carried out a structural optimization. A tetragonal distortion would yield an e_g crystal-field splitting, and if the splitting is big enough, the LS state could become the ground state.

To explore the possibility of the LS ground state, we lower the lattice symmetry to allow a local tetragonal distortion of the AgF_6 octahedra. We first use the above cubic lattice constants but optimize the internal atomic positions under a tetragonal symmetry, by minimizing the atomic forces[27] till each one being smaller than 25 meV/Å. After a full electronic and atomic relaxation associated with the initialized LS setup $t_{2g}^6(3z^2 - r^2)^2(x^2 - y^2)^0$ for the formal Ag^{3+} ion, the LS solution is indeed achieved. It is a local minimum of the energy and has an elongated apical Ag-F bondlength of 2.25 Å and a shrinking planar Ag-F bondlength of 1.96 Å (see Table I for the tetragonal phase). Thus, the LS solution is stabilized by the tetragonal distortion (0.29 Å , $2.25/1.96 = 1.15$). Moreover, in this tetragonally distorted structure, the corresponding HS solution turns out to be less stable than the LS state by $441 - 366 = 75 \text{ meV/fu}$, see Table II. However, the tetragonal LS phase is 366 meV/fu higher in energy than the above cubic HS

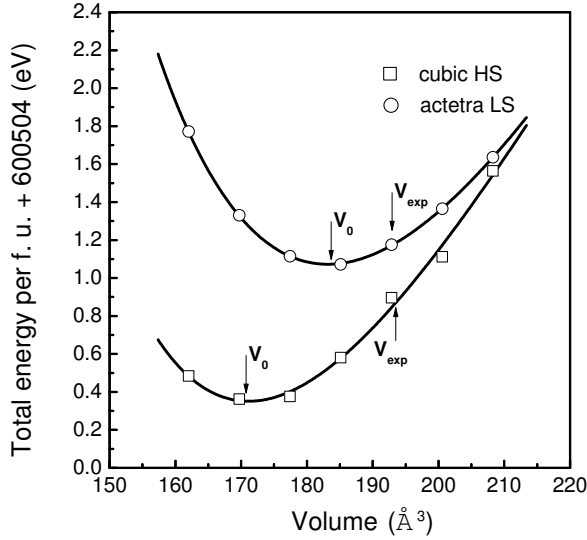


FIG. 4: Volume optimization of the cubic HS phase and the tetragonal LS phase by LSDA+U.

one. We further calculated a regular tetragonal structure with c_0/a_0 [i.e., $c/(\sqrt{2}a)$] = 1.15, see Table I for the ac-tetragonal structure which preserves the volume of the experimental cubic cell and the above tetragonal distortion. This ac-tetragonal LS phase turns out to be still higher in energy than the cubic HS phase by 336 meV/fu.

Now we carry out a volume optimization for both the cubic HS state and the ac-tetragonal LS state. The results are shown in Fig. 4. The equilibrium volume of the cubic HS state is about 11% smaller than the experimental one (i.e., within 4% underestimation of the lattice constant, within a few percent error bar of density-functional calculations). The equilibrium volume of the ac-tetragonal LS state is also 5% smaller than the experimental one. Note that the energy difference between the two equilibrium states, the cubic HS and the ac-tetragonal LS states, increases up to 750 meV/fu. This indicates that the cubic HS ground state is robust against the structural optimization. The metastable LS state is stabilized by the tetragonal distortion, which could be realized in a biaxial pressure experiment. The present bistable HS and LS solutions can also be understood by a pseudo Jahn-Teller mechanism for an e_g^2 system[28].

Before analyzing the reason why the cubic HS phase is the ground state, we now have a close look at the tetragonal phase either in the LS or HS state. In the tetragonal LS state, the degeneracies of both e_g and t_{2g} states are lifted, see Fig. 5. The threefold degenerate t_{2g} states are split into doubly degenerate (d_{xz}/d_{yz}) states and singlet d_{xy} state. Similarly, the twofold degenerate e_g states split into nondegenerate $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states. It is also an insulator with a small band gap of 0.1 eV, which lies between the occupied $pd\sigma$ antibonding band of the $d_{3z^2-r^2}$ orbital and the unoccupied $pd\sigma$ antibonding band of the $d_{x^2-y^2}$ orbital. The equal occupation of the spin-up and spin-down orbitals results in a nonmagnetic state without any exchange splitting, in accordance with the LS $S=0$ character. Note that the strong hybridization be-

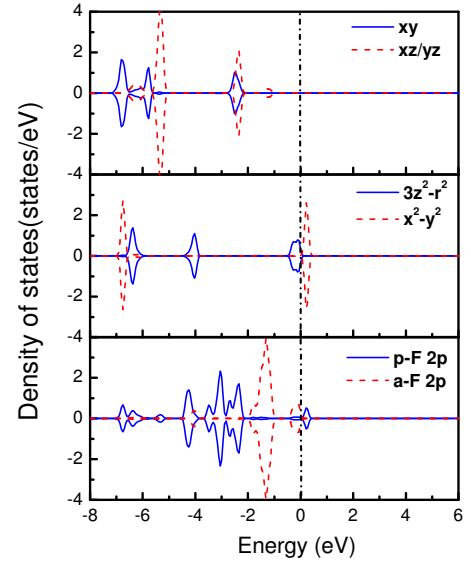


FIG. 5: (color online) The density of states of Ag-4d and planar/apical F-2p orbitals for the tetragonal LS phase of Cs_2KAgF_6 by LSDA+U.

tween Ag 4d and planar-F/apical-F 2p orbitals is similar to that in cubic phase (see Table II), by which the Ag 4d orbitals split into a series of narrow bonding and antibonding orbitals. Such electronic structure, with narrow-band and large bonding-antibonding splitting, is governed by the behavior of the isolated AgF_6 clusters. Generally speaking, the bonding-antibonding splitting of both e_g orbitals is larger than that of t_{2g} orbitals due to larger overlap between e_g and p orbitals. Furthermore, the bonding-antibonding splitting of $d_{x^2-y^2}$ orbital in the tetragonal phase is larger than that of $d_{3z^2-r^2}$ due to the shrinking planar Ag-F bond length. The t_{2g} and $d_{3z^2-r^2}$ bands are fully occupied and the $d_{x^2-y^2}$ band is half occupied. Hence, the 4d occupation of 9e is one more electron than the nominal value for Ag^{3+} . This suggests the strong covalent nature of the Ag-F bonds, in contrast to the naive ionic picture.

For the spin-polarized HS state of the tetragonal phase (Fig. 6), the band splitting and Ag-F hybridization are similar to those in the LS state, but the occupation of e_g orbitals has a remarkable change. While the up-spin $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states are fully occupied, their down-spin counterparts are half occupied. The unequal occupation of the up-spin (5e) and down-spin (4e) states results in a considerable exchange splitting, reflecting a HS state character. Although the double degeneracy of e_g orbitals is lifted by the tetragonal distortion, the electron configuration of $(d_{x^2-y^2})^{0.5}$ and $(d_{3z^2-r^2})^{0.5}$ for down-spin is the same as that in cubic phase with e_g degeneracy, indicating again the significant Ag-F covalency. A tiny band gap lies between the occupied $pd\sigma$ antibonding band of the $d_{x^2-y^2}$ orbital and the unoccupied $pd\sigma$ antibonding band of the $d_{3z^2-r^2}$ orbital.

Here we clarify the reason why the cubic HS phase is the lowest energy state, using the above total-energy results (see Table II). The 441 meV/fu increase of energy from the cubic HS phase to the tetragonal HS phase is attributed to the lattice

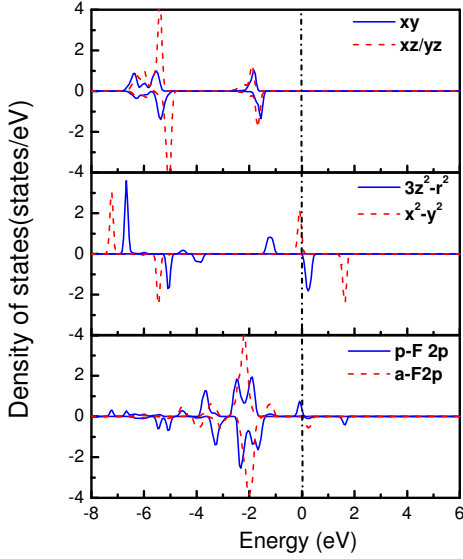


FIG. 6: (color online) The density of states of Ag-4d and planar/apical F-2p orbitals for the tetragonal HS phase of Cs_2KAgF_6 by LSDA+U.

elastic energy cost (E_{el}) associated with the tetragonal distortion, as the electronic configuration remains unchanged in both HS states and no crystal-field energy is involved. The energy difference of 75 meV/fu between the tetragonal HS and tetragonal LS (both in the same lattice) is due to the competition between the Hund exchange (J_H) and the crystal-field level splitting (E_{CF}) of the e_g electrons, with E_{CF} and J_H being both about 1 eV and E_{CF} slightly larger than J_H . Whether the cubic HS phase or the tetragonal LS one is the ground state depends on three competing contributions: $\Delta E = E(\text{tetragonal LS}) - E(\text{cubic HS}) = E_{el} + J_H - E_{CF}$. Taking $J_H - E_{CF} = -75$ meV/fu from above, the tetragonal LS phase could become the ground state ($\Delta E < 0$) only when the E_{el} is lower than 75 meV/fu. However, here E_{el} is up to 441 meV/fu. Therefore, the cubic HS phase is the ground state, and the large elastic energy cost in this compact double perovskite structure prevents the tetragonal distortion from yielding a large E_{CF} to stabilize the LS state.

As seen in Figs. 5 and 6, in the tetragonal phase, the e_g crystal-field splitting and the exchange splitting are quite close in size. This explains the small band gap present in both the LS and HS solutions. This also accords with the small energy difference of 75 meV/fu between the tetragonal HS and LS phases. As discussed above, three competing contributions get involved in determination of the ground spin-state solution: $\Delta E = E(\text{tetragonal LS}) - E(\text{cubic HS}) = E_{el} + J_H - E_{CF}$. Among them, the lattice elastic energy cost E_{el} and the e_g crystal-field splitting E_{CF} are most influenced by the structural details, but the Hund exchange J_H is almost a constant, being about 1 eV. Therefore, only a large E_{CF} but a small E_{el} would favor a tetragonal LS ground state. We thus conceive that such a situation could be met in an open structure, which can maintain a large Jahn-Teller distortion (and thus a large E_{CF}) but with a low E_{el} cost. For example, in

the well-known La_2CuO_4 , there is a huge distortion (0.5 Å) of the Cu-O bonds, being $1.90 \text{ Å} \times 4$ in plane and $2.40 \text{ Å} \times 2$ out of plane[29]. This is due to a lattice strain effect in this layered material[30] and to the Cu-O bondlength adjustment for the $x^2 - y^2$ type hole-orbital order driven by an anisotropic crystal field[31, 32]. Upon a hole doping, the holes spread over the in-plane ligand oxygens and they hybridize with the central Cu^{2+} $S=1/2$ to form a Zhang-Rice singlet[33] (the $d^9 \underline{L}$ configuration with $S=0$ or a nominal LS Cu^{3+} with two holes on $d_{x^2-y^2}$ orbital). It is the large e_g crystal-field splitting but a small elastic energy cost which lead to the formation of the LS state upon hole doping. We can expect to have a similar situation in the layered 214 structure with Ag instead of Cu. However, in the compact perovskite structure of Cs_2KAgF_6 , the tetragonal distortion cannot be as large as in the layered La_2CuO_4 . As a result, here the LS state is disfavored, but the magnetic HS state of the Ag^{3+} ion is the ground state.

IV. CONCLUSIONS

To summarize, using first-principles calculations, we find that the cubic double perovskite Cs_2KAgF_6 has a strong Ag-F covalency, and that the formal Ag^{3+} ion has an unusual high-spin (HS) $S=1$ ground state. This is in sharp contrast to a common view that Ag^{3+} always prefers a tetragonal or lower-symmetry coordination and a low-spin (LS) $S=0$ state. In calculations, we could also get the "normal" LS state, associated with a tetragonal distortion of 0.29 Å. However, the tetragonal LS state turns out to be energetically less favorable than the cubic HS state. We propose that three competing contributions tip the balance between the HS and LS states, which is formulated by the expression $\Delta E = E_{LS} - E_{HS} = E_{el} + J_H - E_{CF}$. As the compact perovskite structure of Cs_2KAgF_6 allows only a moderate tetragonal distortion (but with a large elastic energy cost E_{el}), a corresponding moderate crystal-field energy gain E_{CF} in the tetragonal LS state cannot compensate for the E_{el} and Hund's exchange loss J_H . As a result, the cubic HS phase is the ground state. We thus conclude that Cs_2KAgF_6 is a rare case of the magnetic Ag^{3+} ion, and suggest that the Ag^{3+} LS nonmagnetic state can readily be formed in open structure materials such as layered systems.

V. ACKNOWLEDGMENTS

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